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(54) THERMOPLASTIC ELASTOMER COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a new thermoplastic elastomer composition which has rich flexibility, excellent formability and excellent compression permanent set. SOLUTION: This thermoplastic elastomer composition comprises (A) an isobutylene block copolymer comprising (a) an isobutylene polymer block having a silicone group bound to a hydrolysable group or hydroxyl group at the terminal and (b) a polymer block consisting mainly of an aromatic vinyl compound, and (B) an olefin resin. The composition preferably comprises 100 compound of the component (A) and 10 to 200 pts.wt. of the component (B). The composition is preferably cross-linked, when the components (A) and (B) are melted and kneaded.

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CLAIMS

the olefin system resin (B) of the 10 – 200 weight section to the isobutylene system block-copolymer (A) 100 weight section.

[Claim 3] A thermoplastic-elastomer constituent given in claims 1 and 2 over which a thermoplastic-elastomer constituent constructs a bridge dynamically at the time of melting kneading of an isobutylene system block copolymer (A) and olefin system resin (B). Claim 4] Furthermore, the thermoplastic-elastomer constituent according to claim 1 to 3 which contains a silanol condensation catalyst as a (C) component.

[Claim 5] Furthermore, the thermoplastic-elastomer constituent according to claim 1 to 4 which contains a plasticizer as a (D) component.

[Claim 6] The thermoplastic-elastomer constituent according to claim 5 which carries out 10–300 weight section content of the plasticizer (D) to the total quantity 100 weight section of (A) and (B).

300 weight section content of the plasticizer (D) to the total quantity 100 weight section or (Λ) and (B). (Claim 7) An isobutylene system block copolymer (A) is a thermoplastic-elastomer constituent according to claim 1 to 5 which number average molecular weight is 2000–100,000, and is the block copolymer which has the silicon radical combined with at least one hydroxyl group per molecule at the end. (Claim 8) the polymer block (a) whose isobutylene system block copolymer (A) which has at the end the silicon radical combined with the hydroxyls nature machine or the hydroxyl group makes an isobutylene a subject, and the polymer block (b) which makes an aromatic series vinyl system compound a subject — (b)-(a)- the thermoplastic-elastomer constituent according to claim 1 to 3 which is the triblock copolymer in which the structure of (b) is shown.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Detailed Description of the Invention of the Invention relates to the new thermoplastic-elastomer constituent which was rich in flexibility, was excellent in fabrication rature, the rubber-property, and the mechanical strength, and was excellent in the compression set property.

[Description of the Prior Art] Conventionally, what blended the cross linking agent, the reinforcing agent, etc. with rubber, such as natural rubber or synthetic rubber, and constructed the bridge under elevated-temperature high pressure as polymeric materials which have elasticity is used widely. However, with such rubber, the stroke which performs bridge formation elasticity is used widely. However, with such rubber, the stroke which performs bridge formation and shaping over long duration under elevated-temperature high pressure is required, and it is inferior to workability. Moreover, since the rubber which constructed the bridge does not show thermoplasticity, generally recycle shaping is impossible for it like thermoplastics. Therefore, the thermoplastic elastomer which can manufacture mold goods easily like usual thermoplastics using general-purpose melting forming technique, such as heat press forming, injection molding, and extrusion molding, is developed variously in recent years. The polymer of various formats, such as current, an olefin system, an urethane system, an ester system, a styrene system, and a vinyl chloride system, is developed and marketed by such thermoplastic elastomer. Since recycle use is easy for these, they are used in recent years in broad fields, such as autoparts, household-electric-appliances components, wire covering material, medical components, miscellaneous goods, and footwear.

household-electric-appliances components, wire covering material, medical components, miscellaneous goods, and footwear.

[0003] A styrene thermoplastic elastomer is rich in flexibility, and excellent in good rubber elasticity with ordinary temperature. [among these] As a styrene thermoplastic elastomer, the styrene-budded copolymer (SBS), the styrene-isoprene-styrene block copolymer (SIS), a styrene-ethylene butylene-styrene block copolymer (SESS) has the styrene-styrene block copolymer (SESS), a styrene-ethylene propylene-styrene block copolymer (SEPS) that hydrogenated them, etc. are known. However, these block copolymers had the inadequate compression set property.

[0004] The isobutylene system block copolymer which contains the polymer block which makes an isobutylene a subject and the polymer block which makes an aromatic series vinyl system compound a subject as what was rich in flexibility, was excellent in good rubber elasticity with ordinary temperature, and was further excellent in thermal stability, weatherability, vibration-deadening nature and gas barrier property, and sealing performance also in the styrene ordinary temperature, and was further excellent in thermal stability, weathersouncy, van audo-deadening nature and gas barrier property, and sealing performance also in the styrene thermoplastic elastomer is known. However, this isobutylene system block copolymer also hap problem in the compression set.

thermoplastic elastomer is known, nowever, una isobusyere system and the technique made to compound-ize por high-performance-izing of thermoplastic elastomer it is known for many years. To polyolefines, such as EPDM and IIR, Or about the technique of making the bridge formation object of styrene system elastomers, such as EPDM and IIR. Or about the technique of making the bridge formation object of styrene system elastomers, such as SEBS, compound-tzing, it succeeds in many examination. In the case of thermoplastic elaston clefin, for example, crystalline olefine resin and olefin system rubber The technique (JP,53–21021,8) which constructs a bridge using organic peroxide, the technique which constructs a

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subject, monomers, such as aliphatic series olefins, dienes, allyl compound ether, and beta sugect, monomers, such as aliphatic series olefins, dienes, allyl compound ether, and betarpinene, can be illustrated. As an aromatic series vinyl system compound of a polymer block (b),
styrene, alpha methyl styrene, beta-methyl styrene, p-methyl styrene, t-butyl styrene,
monochlorostyrene, dichloro styrene, methosy styrene, an indene, etc. are mentioned. Also in the
abover-mentioned compound, styrene, alpha methyl styrene, p-methyl styrene, and an indene are
desirable from the balance of cost, physical properties, and productivity, and you may also
choose two or more sorts from them. Especially if monomers other than an isobutylene under
polymer block which makes an aromatic series vinyl system compound a subject are monomer
components in which the abover-mentioned cationic polymerization is possible, they will not be
limited, but they may be used independently, and two or more sorts may be combined and they
may be used.

may be used.

[0013] it is related with the rate of the polymer block (b) which makes a subject the polymer block (a) which makes a subject the isobutylene in an isobutylene system block copolymer (A), and an aromatic series vinyl compound. Although there is especially no limit, the polymer block (a) which makes an isobutylene a subject from the balance of physical properties and workability 95 – 20 weight section, it is desirable that the polymer block (b) which makes an aromatic series vinyl compound a subject is 5 – 80 weight section. It is desirable that the polymer block (b) whose polymer block (a) which makes an isobutylene a subject makes a subject 90 – 60 weight section and an aromatic series vinyl compound is especially 10 – 40 weight section.

[0014] Moreover, the structure which consists of at least one of the polymer blocks (a) which make an isobutylene a subject from the polymer blocks (b) which make an aromatic series vinyl system compound a subject as desirable structure of the isobutylene system block copolymer (A) of this invention is desirable. The above — structure — ****** — especially — a limit — there is nothing — although — for example — (— b —) — (— a —) — (— b —) — from — forming — having — a triblock — a copolymer — (— b —) — (— b —) — in from — forming — having — a triblock — a copolymer — (— b —) — the jib which consists of (a) — at least one sort chosen from the star—like polymer which uses a lock copolymer as an arm can be used. furthermore, the polymer which makes an isobutylene system block copolymer (A) in addition to the above —mentioned structure, the polymer which makes an isobutylene subject into an isobutylene system block copolymer (A) in addition to the above —mentioned structure, the polymer which makes an isobutylene subject the lib which consists of (b) — at least one sort of a lock copolymer may be contained. However, it is desirable that the thing of the structure which consists of the least one of the polymer blocks (b) which make an aromatic series vinyl system com [0013] It is related with the rate of the polymer block (b) which makes a subject the polyr

workability. (0015) Although there is especially no limit also in the number average molecular weight of an isobutylene system block copolymer (A), 1,000-500,000 are desirable, and 2,000 to especially 100,000 is good ****. The fall of a moldability etc. is large when a mechanical property etc. is not fully discovered when number average molecular weight is less than 1,000, and exceeding not fully 500,000.

500,000.

[0016] The silicon radical combined with the hydrolysis nature machine or the hydroxyl group at the end expresses the radical which has Si-X association, when for example, a hydrolysis nature machine or a hydroxyl group is set to X. Usually, Si-OH and H-X are given by the hydrolysis reaction of Si-X association.

[0017] These silicon radical is a functional group known well, and is (general formula D:-(SiR12-bXb0) m-SiR23-aXs (f) as the example of representation.

Each of R1 and R2 among (type The alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20. The aratlyl radical or R33SiO of carbon numbers 7-20 - (R3 is the univalent hydrocarbon group of carbon numbers 1-20) three R3 — being the same — differing - **** — it is the Tori ORGANO siloxy radical shown, and when R1 or two or more R2 exist, they may be the same and may differ. X is a hydrolysis nature machine or a hydroxyl group, and when two or more pieces exist, they may be the same and may differ, a is an integer chosen

bridge using phenol resin (JP,58-46138,B), Although the technique (JP,11-166075,A, JP,11-181172,A) which constructs a bridge using a hydrosilyl radical is reported and use (JP,9-137007,A) of special structure isobutylene rubber is reported All used the olefin system rubber which a double bond exists at random as a point constructing a bridge, such as EPDM and IIR, into the olefin system polymer as a rubber component, its bridge formation was uneven, and the reduction in a degree of hardness was difficult for them. [0006]

reduction in a degree of hardness was difficult for them.
[0006] [Problem(s) to be Solved by the invention] In view of the technical problem of the above—
mentioned conventional technique, the purpose of this invention is rich not only in thermal
stability and weatherability characteristic of a polyisobutylene segment, vibration-deadening
nature, and gas barrier property but flexibility, and is to offer the thermoplastic—elastomer
constituent excellent in fabrication nature, especially a compression set property.

[0007]
[Means for Solving the Problem] That is, this invention is a thermoplastic-elastomer constituent containing the isobutylene system block copolymer (A) containing the polymer block (b) which makes a subject the isobutylene system polymer block (a) and aromatic series vinyl system compound which have at the end the silicon radical combined with the hydrolysis nature machine or the hydroxyl group, and olefin system resin (B), and it is desirable to contain the olefin system resin (B) of the 10 – 200 weight section to the isobutylene system block-copolymer (A) 100 mainter earlier.

weight section. [0008] Said thermoplastic-elastomer constituent can construct a bridge dynamically at the time of melting kneading of an isobutylene system block copolymer (A) and olefin system resin (B). As a constituent, further, as a (C) component, a silanol condensation catalyst can be contained and a plasticizer can also be contained as a (D) component. As for said plasticizer (D), it is desirable to carry out 10-300 weight section content to the total quantity 100 weight section of (A) and (2)

[0009] Moreover, the number average molecular weight of an isobutylene system block copolymer (A) is 2000–100,000. It is desirable that it is the block copolymer which has per molecule the silicon radical combined with at least one hydrolysis nature machine or a hydroxyl group at the end, the polymer block (a) which makes an isobutylene a subject as structure of an isobutylene system block copolymer (A), and the polymer block (b) which makes an aromatic series viryl system compound a subject — (b)–(a)– it is desirable that it is the triblock copolymer in which the structure of (b) is shown. [0010]

[0010]
[Embodiment of the Invention] The thermoplastic-elastomer constituent of this invention comes to contain the isobutylene system block copolymer (A) and olefin system resin (B) containing the polymer block (b) which makes a subject the isobutylene system polymer block (a) and aromatic series vinyl system compound which have at the end the silicon redical combined with the hydrolysis nature machine or the hydrolysi group.
[0011] The polymer block (a) which makes a subject the isobutylene of the isobutylene system block copolymer (A) of this invention means the block with which an isobutylene occupies 90 % of the weight or more more preferably 70% of the weight or more 50% of the weight or more. Although monomers other than an isobutylene under polymer block which makes an isobutylene a subject will not be limited especially if they are monomer components in which cationic polymerization is possible, they can illustrate monomers, such as dienes, such as aromatic series vinyl, alighatic series olefins, an isopreme, a butadene, and a dwinylbenzene, allyl compound ether, and beta-pinene. These may be used independently, and two or more sorts may be combined and they may be used.

euter, and beta-prene. I ness may be used independently, and two or more sorts may be combined and they may be used. [0012] The polymer block (b) which makes a subject the aromatic series vinyl system compound of an isobutylene system block copolymer (A) means the block with which an aromatic series vinyl system compound occupies 90 % of the weight or more more preferably 70% of the weight or more 50% of the weight or more. Although there will be especially no limit if it is the monomer in which cationic polymerization is possible as monomers other than the aromatic series vinyl compound under polymer block which makes an aromatic series vinyl system compound a

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from 0-3, and b is an integer chosen from 0-2. However, a+mb>=1 is filled. Moreover, b in m

desirable. [0021] A reactant silicon radical is averaged per molecule of an isobutylene system copolymer, its at least one piece is desirable, and its 1.1-5 pieces are still more desirable. If the number of the reactant silicon radicals contained in a molecule becomes less than one piece, cross-linking will become inadequate and will stop being able to discover good nubber elasticity behavior easily. The reactant silicon radical may exist in both. Since the effective network chain density of the isobutylene system copolymer chain, may exist in the interior, and may exist in both. Since the effective network chain density of the isobutylene system copolymer component contained in the bridge formation object finally formed increases in having at least one of a reactant silicon radical at the chain end especially, it is desirable from points, like the nubber-like bridge formation object finally intensity becomes is easy to be obtained. Moreover, the isobutylene system copolymer which has these reactivity silicon radical may be used independently, and may be used together two or more sorts.

more sorts. [0022] After carrying out a polymerization with iniphor method in the case of an isobutylene system copolymer, it is known that many functional groups can be introduced. For example An alkenyl radical (JP,63–105005A, JP,1–248406A, WO 90/15081, JP,4–288309A, etc.), (Meta) serylic radicals (JP,2–88814A, etc.) and a hydroxyl group (Ivan et al. —) J. Polymer Sci. Polymer Chem. Ed. 18 3177 (1980), JP,4–20501A, JP,11–302320A, JP,2000–193330A, JP,2000–103810A, etc. are illustrated by carbonyl groups (JP,2000–150076A, JP,2000–159518A, etc.) and gyicityl groups (JS, Pat. No. 4429099 etc.).
[0023] And it is possible to compound assily the organic polymer which has hydrolysis nature sificon radicals (JP,63–006041A, JP,63–6003A, JP,1–197509A, JP,4–103606A, JP,7–53882A, tot.) at the molecule and based on the functional group by which installation was carried out

etc.) at the molecule end based on the functional group by which installation was carried out nentioned 1.

[0024] Moreover, the isobutylene system copolymer which has a reactant silicon radical in intramolecular is manufactured by adding and carrying out copolymerization of the vinyislane and arytailane which have a reactant silicon radical into the monomer which is mainly concerned with an isobutylene. Furthermore, the isobutylene system copolymer which has a reactant silicon radical at both the interior of a molecule and the molecule end can be manufactured by introducing a reactant silicon radical into an end, after carrying out copolymerization of the vinyislane and arytislane etc. which have a reactant silicon radical in addition to the monomer which constitutes a principal chain in the polymerization at the time of manufacturing the isobutylene system copolymer which has a reactant silicon radical at the above-

isobutylene system copolymer which has a reactant silicon radical at the above-mentioned molecule end. [0025] The olefin system resin (B) used by this invention is ethylene, the alpha olefin homopolymer whose content of the alpha olefin of carbon numbers 3-20 is \$0 - 100-mol %, or a copolymer, and polypropylene, ethylene propylene rubber, EPR EPDM, an ethylene butter copolymer, polypropylene, ethylene propylene rubber, EPR EPDM, an ethylene butter copolymer, an ethylene octene copolymer, a polyisobutylene, isobutylene isoprene rubber, chlorinated butyl rubber, brominated butyl rubber, and the physical-properties target. [0026] As for the loadings of olefin system resin (B), it is desirable that it is the 10 - 200 weight section to the isobutylene system block-copolymer 100 weight section of a component (A), and it is still more desirable that it is the 20 - 100 section. When the loadings of olefin system resin (B) exceed the 200 weight sections, it is in the inclination for an improvement of a component (A) and it is still more desirable that it is the 20 - 100 section. When the loadings of olefin system resin (B) of a component (A), what constructed the bridge independently, (0027) As for the thermoplastic-clastomer constituent which consists of the isobutylene system block copolymer and olderin system resin (B) of a component (A), what constructed the bridge dynamically at the time of melting kneading is desirable. [0028] the bridge formation formed here — the inside of the body — (A) or (B) — the object with which either constructed the bridge independently, (A), and (B) — coincidence — bridge formation — the object which was contained inside of the body and constructed the bridge is contained. It is desirable to form a bridge formation object by the (A) independent among these. [0029] The property which the hydrolysis radical combined with the silicon radical on which the isobutylene system copolymer which its the (A) component has the cross-linking constituent of this invention, it is possible to add a sil

dilustrated.

(10031) As an example of said tetravalent tin system condensation catalyst, tetravalent tin carbonylate, such as dibutyttin bisacetylacetonate, dibutyl SUZUJI alkoxide, dibutyltin dilaurate, dibutyltin maleate, and dibutyltin disacetate, is raised, for example, moreover, as an example of silanol condensation catalysts other than the tin system condensation catalysts of the abover-mentioned tetravalence Divalent tin system condensation catalysts, such as octylic acid tin; Tetrabuthyl titanate, Titanate, such as tetra-propyl titanate; Aluminum tris acetylacetonato, Aluminum system condensation catalyst; zirconium tetrapod acetylacetonato; lead octylate, such as aluminum tris ethyl acetoacetate and JISOPUROPO(ISIAI) aluminum ethyl acetoacetate; A butylamine, An octyl amine, a lauryl amine, dibutyl amine, monoethanolamine, Diethenolamine, triethylenetriamine, diethylenetriamine, Triethylenetetramine, an oleyl amine, cyclohexylamine, Benzylamine, diethylamino propylamine, riethylenetamine, Triethylenediamine, guanidine, diphenylguanidine, 2 and 4, 6-tris (dimethyl aminomethyl) phenol. They are amine system condensation catalysts, such as morpholine, N-methyl morpholine, 2-ethyl-4-methylimidazole, 1, and 8-diazabicyclo (5, 4, 0) undecene -7 (DBU).

condensation catalysts, such as morpholine, N-methyl morpholine, 2-ethyl-4-methylimidazole, 1, and 8-diazabicyclo (5, 4, 0) undecene -7 (DBU). [0032] Although a silanol condensation catalyst is freely chosen according to a service condition, the tin system compound from the field of storage stability, and a cure rate and availability, especially its dibutly tin compound are desirable. The above-mentioned silanol condensation catalyst may be used only by one kind, and may carry out two or more kind mixing use. As for a

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such as a methoxy group, an ethoxy radical, a propoxy group, and an oxime radical, is illustrated, such as a methory group, an ethory radical, a propoxy group, and an oxime radical, is illustrated, for example, Although there is no limit especially in the usable range as functional groups other than the silyl radical which exists in a hydrotysis nature machine content silane compound, a vinyl group, an methacrylic radical, an acrylic radical, a sufflydryl group, a hydroxyl group, an isocyanate radical, the animo group, an amide group, a glycidyl group, etc. make it tillustrate. As a more concrete example, ethyl silicate, a silicate condensate, vinyltrimetoxysilane, 3-methacryloxy propyl trimethoxysilane, 3-aminopropyl trimethoxysilane, 3-methoryloxy propyl trimethoxysilane, 3-aminopropyl trimethoxysilane, N-methyl-3-aminopropyl trimethoxysilane, N-methyl-3-aminopropyl trimethoxysilane, N-methyl-3-aminopropyl trimethoxysilane, N-methyl-3-aminopropyl trimethoxysilane, N-methyl-3-isocyanato propyltrimethoxysilane, 3-isocyanato propyltrimethoxysilane, 3-isocya

[0038] As for the above-mentioned silane compound, it is desirable to use it in the range of the 0.01 - 50 section to the isobutylene system (copolymer A) 100 section which has a reactant silicon radical. It is desirable to use it in the range of the one to 10 section further the 0.1 to 30 section especially.

(0037) The above-mentioned silane compound may be used only by one kind, and may carry out two or more kind mixing use. For example, silicate from the semantics of storage stability, vinytrimetoxysilane. One or more sorts of compounds chosen from 3-methacryloxy propyl trimethoxysilane are used. From the field of adhesive grant to furthermore, 3-aminopropyl trimethoxysilane are used. From the field of adhesive grant to furthermore, 3-aminopropyl trimethoxysilane. The operation of using one or more sorts of compounds chosen from 3-incorpants propyl trimethoxysilane, 3-aminopropyl triethoxysilane. N-floeta-aminocityl) aminopropyl methyl dimethoxysilane, The operation of using one or more sorts of compounds chosen from 3-isocyanot propyl trimethoxysilane, 3-isocyanato propyl triethoxysilane, and 3-glycidyl propyltrimethoxysilane is also possible. The olefin system resin which has the silicon radical combined with the hydrolysis nature machine or the hydroxyl group may be added. A graft polymer generates by the reaction in a system with the isobutylene system block copolymer of a component (A). Consequently, an improvement of the compatibility of the isobutylene system block copolymer of a component (A) and the polylosfine system resin of a component (B) is expectable. As polylosfine in this component, the polymer of structure which may be compatible in the olefin system resin of a component (B). As olefin system resin of a component (B), since polypropylene is desirable, and it is desirable that it is especially the same structure as a component (B). As olefin system resin of a component (B), since polypropylene is desirable, only in the polylosfine in this component. Although some which are marketal have as

silanol condensation catalyst, it is desirable to use it from the standpoint of a bridge formation rate or storage stability in the range of the 0.01 – 50 section to the isobutylene system (copolymer A) 100 section which has a reactant silicon radical. It is desirable to use it in the range of the 0.1 to 5 section further the 0.1 to 30 section especially. In order to raise a moltability and flexibility further in the constituent of this invention in addition to the isobutylene system block copolymer of a component (A), offer system resin (B), and a silanol condensation catalyst (C), to it, it is desirable to add a plasticizer (D) further.

[0033] That there is no limit in the range appropriate for the purpose of this invention as a plasticizer (D) For example, polybutene, hydrogenation polybutene, hydrogenation alphanel olefin oligomer, Polyvinyl system oligomer, such as a stactic polypropylene, A bipheryl, triphenyl etc. — etc. — aromatic series system oligomer; — polypene system oligomer [, such as invented polybutadiene,]; — hydrogenation polypene system oligomer [, such as a chlorogenation ilquid polybutadiene,]; — a paraffin oil — paraffin series oligomer [, such as a chlorogenation ilquid polybutadiene,]; — a paraffin oil — paraffin series oligomer [, such as a chlorogenation ilquid polybutadiene,]; — a paraffin oil — paraffin series oligomer [, such as a chlorogenation ilquid polybutadiene,]; — a paraffin oil — paraffin series oligomer [, such as a chlorogenation ilquid polybutadiene,]; — a paraffin oil — paraffin series oligomer [, such as a chlorogenation oliquid polybutadiene,]; — a paraffin oil — paraffin series oligomer [, such as a chlorogenation ilquid polybutadiene,]; — a paraffin oil — paraffin series oligomer [, such as a scilic polybutadiene,]; — a paraffin oil — paraffin series oligomer [, such as middle of desired polybutadiene,]; — a paraffin oil — paraffin series oligomer [, such as a scilic polybutadiene, different polybutadiene, different polybutadiene, different polybutadiene,

leadings exceed the 300 weight sections, a problem will arise in a fall and moldability of a mechanical strength.

[0034] In addition to the above-mentioned (A) component, the (B) component, the (C) component, and the (D) component, according to the demand characteristics doubled with each application, it can blend with the constituent of this invention as olefin system resin which has the silicon radical combined with the tackifier, the hydrolysis nature mechine content silane compound, as possible to the purpose, it can choose from inside freely, control, etc. and it is generally used, according to the purpose, it can choose from inside freely, for example, a petroleum resin system, a phenol system, a tempene system, a compose resident system, a consider system, a densturation terpone system, a hydrogenation terpone system, a pinene system, a cumarone indene system, styrene systems, those hydrogenation objects, etc. are illustrated. Although other combination presentations and a target property determine the amount of the tackifier used and there is especially no limit in the usable range, it is desirable to use it in the range of the 2 – 1000 section to a total of 100 sections of the (A) component and the (B) component. It is desirable to use it in the range of the ten to 100 section especially.

[0035] A hydrolysis nature machine content silane compound has effectiveness, such as adhesive improvement, and cross-linking, storage stability adjustment, and can be suitably used according to a need property. Although a hydrolysis nature machine content silane compound kind does not have a limit especially in the usable range, a thing with hydrolysis nature machines.

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wder, the Flint powder, zinc dust, wood flour, PARUBU, a cotton chip, asbestos, walnut shell powder, chaff powder, the diatom earth, clay, etc. are usable and are fire-resistant grant, Fire-resistant bulking agents, such as an aluminum hydroxide, a magnesium hydroxide, and ammonium phosphate, can be used. Moreover, hygroscopic bulking agents, such as a zeolite, silica gel, and a molecular sieve, can be used from the purpose of the hygroscopic grant mentioned later. These fillers may be used independently and may be used together two or more sorts.

[0038] As an example of said silane coupling agent gamma-aminopropyl trimethoxysilane. molecular sieve, can be used from the purpose of the hygroscopic grant mentioned later. These fillers may be used independently and may be used together two or more sorts.

[0038] As an example of said silane coupling agent gamma—aminopropyl trimethoxysilane, gamma—aminopropyl triethoxysilane, gamma—aminopropyl methylderboxysilane, gamma—(2-aminopropyl triethoxysilane, gamma—(2-aminopropyl triethoxysilane, gamma—mercapto propyltrimethoxysilane, gamma—mercapto propyltrimethoxysilane, gamma—mercapto propyltrimethoxysilane, gamma—mercapto propyltrimethoxysilane, gamma—mercapto propyltriethoxysilane, gamma—glycidoxy propyltriethoxysilane, gamma—glycidoxy propyltriethoxysilane, gamma—glycidoxy propyltriethoxysilane, gamma—glycidoxy propyltriethoxysilane, gamma—glycidoxy propyltriethoxysilane, gamma—glycidoxy propyltriethoxysilane, gamma—methoxysilane, gamma—dispolated gamma—methoxysilane, gamma—methoxysilane, gamma—methoxysilane, gamma—methoxysilane, gamma—methoxysilane, gamma—methoxysilane, gamma—isoxyanate propyltriethoxysilane, gamma—isoxyanate propyltriethoxy

peroxide. [0042] The constituent of this invention can blend the bridge formation assistant which has an ethylene system partial saturation radical on the occasion of the bridge formation processing by organic peroxide. An ethylene system partial saturation radical is a polyfunctional methacrylate monomer like a timinytenzene, a polyfunctional vinyl monomer like a timinytenzene, a polyfunctional viny

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dimethacrylate, polyethylene glycol dimethacrylate, trimethylolpropanetrimethacrylate, and allyl compound methacrylate etc. These may be used independently or may use at least two or mor sorts. With such a compound, homogeneity and efficient crosslinking reaction are expectable. [0043] in order to be easy to deal with othylene glycol dimethacrylate and triethylene glycol dimethacrylate, to have a peroxide solubilization operation and to work as a distributed assistar of peroxide also especially in it, since the homogeneity and bridge formation thermoplastic elastomer which was effective and was able to balance hardness and nubber elasticity is elastomer which was effective and was able to balance hardness and rubber elasticity is obtained, the bridge formation effectiveness by heat treatment is desirable. The addition of the above-mentioned bridge formation assistant has the desirable range of the 0.5 – 10.0 weight section to the isobutylene system block-copolymer denaturation object 100 weight section. If the addition of a bridge formation assistant will not be acquired but 10 weight sections, will be exceeded, there will be a possibility of independent gelation of a bridge formation assistant progressing and bringing about a physical-properties fall, and cost will cost dearly.

[0044] As an example of said phenoic antioxidant 2.6—G t-butylphenol, 2.4—G t-butylphenol, 2.5—G:-t-butylphenol, 2.5—G:-t

(0045) As an example of said aromatic amine system anti-oxidant, it is N and N'-diphenyl-p-phenylene diamine and 6-othoxy. - It is 2, 2, and 4-trimethyl. -A 1 and 2-dihydroquinoline etc. can be illustrated.

can be sustrated.

(D048) As an example of said sulfur system hydroperoxide decomposition agent, dilauryl -3, 3'-thiodipropionate, JITORIDESHIRU -3, 3'-thiodipropionate, distanyl -3, 3'-thiodipropionate, etc.

said Lynn system hydroperoxide decomposition agent. Gut. Can be utarrated as an example of said benzotriazol system utraviolet ray absorbent, 2-(3, 5-G t-butyl-2-hydroxyphenyl)-5-chlorobenzo triazole, 2-(3, t-butyl-2-hydroxyphenyl)-5-chlorobenzo triazole, 2-(3-t-butyl-2-hydroxyphenyl)-5-chlorobenzo triazole, 2-(3, 5-G t-butyl-2-hydroxyphenyl)-5-chlorobenzo triazole, 2-(3-t-butyl-2-hydroxyphenyl)-5-chlorobenzo triazole, 2-(3-t-butyl-2-hydroxyphenyl)-5-chlorobenzo triazole, 2-(3-t-butyl-2-hydroxyphenyl)-5-chlorobenzo triazole, 2-(3-t-butyl-2-hydroxyphenyl)-5-chlorobe

υιαχοιιο, ζ=(3, 3=6 t=buty+=2-hydroxyphenyl) benzotriazol, 2=(5-methyl=2-hydroxyphenyl) benzotriazol, etc. can be illustrated. [0049] As an example of said SARISHI rate system ultraviolet ray absorbent, 4-t-buthylphenyl SARISHI rate, 2, and 4-G t-buthylphenyl-3 and 5 '- G t-butyl-4'-hydroxy benzoate etc. can be illustrated.

[0050] As an example of said benzophenone system ultraviolet ray absorbent, 2, 4-dihydroxy benzophenone, 2-HIDOROKI-4-methoxybenzophenone, 2-HIDOROKI-4-methoxybenzophenone, 2-HIDOROKI-4-mediocyloxy benzophenone, a 2-HIDOROKI-4-benzyloxy benzophenone, etc. be illustrated.

can be ilkstrated.

[0051] As an example of said HINDATO amine system light stabilizer Bis(2, 2, 6, 8, tetramethyl-4-piperidyl) sebacate, Bis(1, 2, 2, 6, 8, - pentamethyl-4-piperidyl) sebacate, I-[2[3-(3, 5-G t-butyl-4-hydroxyphenyl) propionyloxy] ethyll-4-[3-(3, 5-G t-butyl-4-hydroxyphenyl)
propionyloxyl-2, 2, 6 and 6, and - tetramethylpiperidine — 4-benzoyloxy - 2, 2, 6, 6, tetramethylpiperidine, etc. can be ilkstrated.

[0052] As an example of said nickel system light stabilizer, nickel dibutyl dithio carbamate and
[bis[2 and 2-thio] (4-t-cotyl phenolate)]—2-ethylpaxylamine nickel (II) [bis[2 and 2-thio] (4-t-cotyl phenolate)]—1-butylamine nickel (II) etc. can be ilkstrated.

[0053] Those antioxidants may be used independently and may be used together two or more
sorts. As compared with the case where it is used independently, it may function more
effectively by using together.

sorts. As compared with the case where it is used independently, it may function more effectively by using together.

[0054] this invertion — thermoplastic elastomer — a constituent — most — being desirable — a constituent — ******* — an end — hydrolysis — a sex — a machine — or — a hydroxyl group — having joined together — silicon — a radical — having — an isobulytene — a system — a polymer — a block — (— a —) — aromatic series — vinyl — a system — a compound — a

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press forming, blow molding, etc.

[0061] The cross-linking constituent of this invention is available for garments and footwear applications, such as a food-grade way, the miscellaneous-goods application for days, a toy, movement and a sporting gear application, a stationery application, an automatic in-the-car sheathing application, engineering works and a building use. AV and a household-electrical applicances device application, OA and a business machine application, and an object for electrical and electric equipment, a textile application and electric equipment, a textile application, an electric-wire application, etc.

[0062] Specifically the thermoplastic-elastomer constituent of this invention it excels in flexibility, the moldability, and the compression set property. A sheet, a Plastic solid, it is fabricated by a viscous element, foam, etc. Sheets, such as an engineering-works sheet and a tarpaulin, Seal material, such as a packing material, a sealant, a gasket, and a plug, a structural damper. An automobile, a car, the sound deadener for home electronics and vibroisolating material that are called CD damper, A medical-application cast heter, a medical container, a medical-application cap, a paper diaper, sanitary items, it can be effectively used as wire covering material, a cable, a connector, a plug, automobile interior material, the shaping material for automobiles, other various containers, a cushoning material, grip material, shock absorbing material, a packing material, an asphalt modifier, and a resin modifier.

[0063]

[Example] Although this invention is further explained below at a detail based on an example, this

[0063]
[Example] Although this invention is further explained below at a detail based on an example, this invention does not receive a limit at all by these. In addition, in advance of an example, various measuring methods, an appraisal method, and an example are explained.
[0064] (Degree of hardness) Based on JIS K 6352, the test piece used 12.0mm ++ press sheet.
[0065] (Compression set) Based on JIS K 6262, the test piece used 12.0mm thickness press sheet. It measured on condition that deformation 100 degree—Cx 22 hours, and 25%. Moreover, the cable address and the concrete contents of the ingredient used for below in the example and the example of a comparison are as follows.
[Component A): SISIBS: The polystyrene-polysisobutylene-polystyrene triblock copolymer which contains a methyl dimethoxy radical in molecule both ends [number average molecular weight 15000 and molecular weight degree of dispersion 1.5]
Component (B): P. P. Polypropylene, Mitsui Chemicals, Inc. make (trade name "the high pole J300")

Component (9) P. Polypropylene, Mitsui Chemicals, Inc. make (trade name "the high pole J300")

(Component C):silanol condensation catalyst: — dibutyftin dilaurate (component E):plasticizer: — paraffin series process oil and Idemitsu petrochemical company make (trade name "Diana process oil PW-90")

SIBS: Polystyrene-polyisobutylene-polystyrene triblock copolymer [number average molecular weight 67000 and molecular weight degree of dispersion 1.5]

([Example 1 of manufacture) Manufacture of the polystyrene-polyisobutylene-polystyrene triblock copolymer (SiSBS) with which the silicon radical combined with the methoxy group was introduced into the end]

A syringe is used after carrying out the nitrogen purge of the inside of the polymerization container of the separable flask of 2L n-hexane (what was dried by molecular sieves) 456.1mL, and butyl chloride (what was dried by molecular sieves) 655.5mL are added. After attaching a polymerization container all over ~70-degree C for ice / methanol bus and cooling. The liquid-sending tube made from Teffon (trademark) was connected to proof-pressure glass liquefaction extraction tubing with a three-way cock containing isobutylene monomer 201mL (213mml), and the isobutylene monomer was sent by nitrogen pressure in the polymerization container, p-JIKUMIRU chloride 2.6g (11.2mmol) and 1.22g (14mmol) of N.N-dimethylacetamide were added. Next. titanium-tetrachloride 9.9mL, (90.0mmol) was added further, and the polymerization initiation, polymerization solution abbreviation ImL, was sampled as an object for a sampling from the polymerization solution abbreviation ImL, was sampled as an object for a sampling from the polymerization container.

subject — ** — carrying out — a polymer — a block — (— b —) — containing — an isobutylene — a system — a block copolymer — (— A —) — bridge formation — an object — 100 — weight — the section — receiving — an olefin — a system — resin — (— B —) — 20 — 100 — weight — the section — a plasticizer — (— D —) — ten — - 300 — weight — the section — it is .

action — it is .

[0055] Moreover, especially the manufacture approach of the thermoplastic-elastomer constituent of this invention is not limited, but if they are the isobutylene system block copolymer (A) containing the polymer block (b) which makes a subject the isobutylene system polymer block (a) and the aromatic-series vinyl system compound which have the silicon radical combined with the hydrolysis nature machine or the hydroxyl group at the end, olefin system resin (B), and the approach with which the above-mentioned component used by the case may be mixed by homogeneity, it can adopt all.

[0056] When constructing a bridge dynamically in a component (A) and/or olefin system resin (B).

to make by incomparisty, it can adopt as:

(0056) When constructing a bridge dynamically in a component (A) and/or olefin system resin (B) and manufacturing the thermoplastic-elastomer constituent of this invention at the time of melting mixing of a component (A) and olefin system resin (B), it can carry out preferably by the

melting mixing of a component (A) and olefin system resin (B), it can carry out preferably by the approach of illustrating below. (0057) For example, a lab PURASUTO mill, Brabender, a Barbury mixer, a kneader, Atthough manufactured using making machines, such as melting kneading equipment of continuous system, such as direct-vent-system kneading equipments, such as a roll, or batch type kneading equipment, a single screw extruder, and a twin screw extruder, or extrusion modding, injection modding, and compression modding. After carrying out melting kneading adding moisture subsequently to it and crosslinking reaction's fully advancing until it mixes all components beforehand and becomes homogeneity, the approach of stopping melting kneading is employable. In performing the above-mentioned method of performing dynamic bridge formation to melting kneading and coincidence, the temperature of 140-210 degrees C is desirable.

[0058] The constituent of this invention discovers the especially excellent description by making the (A) component construct a bridge by the silanel condensation reaction as mentioned above. It is effective in a silanol condensation reaction in supply of moisture, and although there is especially no limit as the supply approach of the moisture in this invention, after fabricating the approach of supplying moisture, for example just before fabricating to the approach of supplying moisture at the time of kneading of (1) constituent, and the constituent which carried out (2) kneading, at it is the approach of supplying moisture at the time of kneading of (1) constituent, and the constituent which carried out (2) kneading, at it is the approach of supplying moisture at the time of kneading of (1) constituent, and the constituent which carried out (2) kneading, at the constituent which carried out (3) kneading, it is the approach of supplying moisture at the time of kneading of (1) constituent, and the constituent which carried out (2) kneading, at the constituent which carried out (2) kneading, at

desirable.

[0059] Moreover, the various addition approaches can choose, for example, a mixer or the static or high hydrolysis nature machine content silams compound of an approach and temperature dependence which mixes with a mechanical mixer add for moisture and/or a hydrolysis nature machine contents silams compound before kneading, the approach of controlling a reaction by the temperature change and the compound to which water made stick add, and, in the case of the approach of adding moisture etc. before kneading, the approach of controlling a reaction by the temperature change etc. is illustrated. When using the hydrate of a metal salt as a source of supply of required moisture, the hydrate of a metal salt, can use widely what is usually marketed, for example, the hydrate of an alkaline-earth-metal salt and the hydrate of on alkaline-earth-metal salt and the hydrate of an alkaline-earth-metal salt and the hydrate of other metal salts, etc. are mentioned. Also in these, the hydrate of an alkaline-earth-metal salt and the hydrate of an alkaline-earth-metal salt and the hydrate of other metal salts, etc. are mentioned. Also in these, the hydrate of an alkaline-earth-metal salt salts in the second of a component (A. J. Especially, it, is still still more desirable to use it in the range of the two to 10 section the one to 20 section the 0.1 to 30 section. The hydrate of the above-mentioned metal salt may be used only by one kind, and may carry out two or more kind mixing use.

carry out two or more kind mixing use.

[0060] The thermoplastic-elastomer constituent of this invention can be fabricated using the shaping approach and shaping equipment which are generally adopted to a thermoplastics constituent, for example, can carry out melting shaping by extrusion molding, injection molding.

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[0066] 45 minutes after adding this mixed solution, allyl compound trimethyl silane 12ml (10.0mmol) was added. After stirring at temperature as it is for 60 minutes, the methanol of about 40 ml.(s) was added and the reaction was terminated. [0067] After distilling a solvent etc. out of a reaction solution, it dissolved in toluene and rinsing

[0067] After distilling a solvent etc. out of a reaction solution, it dissolved in toluene and rinsing was performed twice. Furthermore, the toluene solution was added to a lot of methanols, the polymer was sattled, and the target block copolymer was obtained by carrying out the vacuum drying of the obtained polymer at 60 degrees C for 24 hours. The molecular weight of the polymer obtained by the gel-permeation-chromatography (GPC) method was measured. Mn of the isobutylene polymer before styrene addition of 10500 and Mw/Mn is 1.40, and the block copolymer whose Mw/Mn Mn of the block copolymer after a styrene polymerization is 15000, and is 1.50 was obtained.

[0068] In this way, 80g and dimethoxymethylsilane 2.8g were made to react among the obtained allyl group end polystyrene-polysisobutylene-polystyrene triblock copolymers. As a catalyst, 5.6mg (0.0000831 mmol/mu L xylene solution) of platinum vinyl siloxene complexes was added. The reaction was performed at 90 degrees C for 8 hours. The polystyrene-polysisobutylene-polystyrene triblock copolymer with which the silicon radical combined with the methoxy group was introduced into the end was obtained after reduced pressure drying.

[0068] [(Example 2 of manufacture) Manufacture of a styrene-isobutylene-styrene block copolymer (SIBS)]

A syringe is used after carrying out the nitrogen purge of the inside of the polymerization

[0069] [[Example 2 of manufacture) Manufacture of a styrene-isobutylene-styrene block copolymer (SIBS)]

A syringe is used after carrying out the nitrogen purge of the inside of the polymerization container of the separable flash of 2L. n-hexane (what was dried by molecular sieves) 456.1mL, and butyl chloride (what was dried by molecular sieves) 555.5mL are added. After attaching a polymerization container all over -70-degree C dry ice / methanol bus and cooling. The liquid-sending tube made from Teflon (trademark) was connected to proof-pressure glass liquefaction extraction tubing with a three-way cock containing isobutylene monomer 232mL (287 Immol), and the isobutylene monomer was sent by nitrogen pressure in the polymerization container, pINLUMIRU chloride 0.6479 (2.8mmol) and 1.22g (14mmol) of N.N-dimethylacetamide were added.
Next. titanium-tetrachloride 8.67mL (79.1mmol) was added further, and the polymerization was started. After agitating at the temperature same for 1.5 hours from polymerization initiation, polymerization solution. Then, the mixed solution of styrene monomer 77.9g (748mmol) beforehand cooled at -70 degrees C, n-hexane 2.37mL, and butyl chloride 34.3mL was added in the polymerization container. 45 minutes after adding this mixed solution, the methanol of about 40 mL(s) was added and the reaction was terminated.

[0070] After distilling a solvent etc. out of a reaction solution, it dissolved in toluene and rinsing was performed twice. Furthermore, the toluene solution was added to a lot of methanols, the polymer was sattled, and the target block copolymer was obtained by carrying out the vacuum drying of the obtained polymer at 50 degrees C for 24 hours. The molecular weight of the polymer obtained by the gel-permeation-chromatography (GPC) method was measured. Mn of the isobutylene polymer before styrene addition of 50,000 and Mw/Mn is 1.40, and the block copolymer whose Mw/Mn Mn of the block copolymer after a styrene polymerization is 67,000.

[Example 1) Adding [carried out methin

and is 1.50 was obtained. (Example 1) Adding [carried out melting kneading of the SiSIBS using the lab PURASUTO mill (Oriental machine company make) which set the 100 sections and PP as the 25 sections, and set these as 170 degrees C, and] water for the plasticizer 150 section and the silanol condensation catalyst 2.5 section gradually subsequently, after carrying out melting kneading, addition and, melting kneading was further carried out at 170 degrees C until the value of torque showed the peak price, and dynamic bridge formation was performed. The obtained thermoplastic-relastomer constituent was able to be easily fabricated at 180 degrees C in the thermoplastic-elastomer constituent was able to be easily fabricated at 180 degrees C in the shape of a sheet with the Shindo metal industry company make and a pressurization press. The degree of hardness and compression set of the obtained sheet were measured according to the abover-mentioned approach. The degree of hardness was 42 and the compression set was 40% (Example 1 of a comparison) After carrying out meting kneeding for 10 minutes using the lab PURASUTO mill which set SIBS as 180 degrees C, it fabricated at 180 degrees C in the shape of a sheet. The degree of hardness of the obtained sheet was 47, and the compression set was 87%.
[0071]
[Table 1]

		実施例1	比較例 1
(A) (£改	SISIBS (減量部)	100	
	SIBS (重量部)		100
成分 (B)	PP (建整部)	2.5	
成分 (C)	シラノール総合触媒(収量部)	2. 5	
庭分 (D)	可抵別(重益部)	150	
	硬度 (ShoreA、直接)	4 2	47
	圧線永久炎(X)	40	8 7

Thus, the thermoplastic-elastomer constituent of an example 1 showed the compression set value quite lower than a SIBS simple substance, though it was a degree of hardness almost equivalent to the SIBS simple substance which is an isobutylene system block copolymer shown in the example 1 of a comparison.

[0072]

[Effect of the Invention] Thus, the thermoplastic-elastomer constituent of this invention is a new thermoplastic-elastomer constituent which was rich in flexibility and was excellent in fabrication nature, especially a compression set property.

[Translation done.]